ROCKET POWER, INC.

A SUBSIDIARY OF THE GABRIEL COMPANY

STUDY OF ROCKET ENGINE EXHAUST PRODUCTS

SIXTH QUARTERLY REPORT
1 September 1962 through 30 November 1962

Contract No. AF 04(611)-7414
Edwards Air Force Base, California

RESEARCH LABORATORIES
3016 E. FOOTHILL BLVD.
PASADENA, CALIFORNIA

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ABSTRACT

During the past three months specially designed apparatus for use in the studies of the thermodynamic properties of BeCl, $BeCl_2$, BeO and Be_3N_2 has been constructed. These items include an electron bombardment furnace-- Southard drop calorimeter combination for the study of the heat capacity and heat of fusion of BeO; an ultra-high vacuum system (10^{-10}mm of Hg) for the study of the vapor pressures of $BeCl_2$ and Be_3N_2; and a vacuum apparatus for the molecular flow effusion study of the thermodynamics of BeCl(g).

Preliminary values for the heat of formation of BeCl(g) and the heat of sublimation of $BeCl_2$ have been obtained.

I. INTRODUCTION

The extensive research and development efforts in the area of high energy propellant systems, solid, liquid and hybrid, have led to consideration of an increasingly large number of compounds containing an ever-widening spectrum of the elements. The accurate theoretical evaluation of these new propellant systems in terms of specific impulse, range and similar parameters, requires a knowledge of the thermodynamic properties of the reactants (heat of formation, ΔH_f, is the prime requisite here) and the thermodynamic and physical properties of all the possible products. Among the values needed are heat of formation, entropy, heat capacity, melting point, boiling point, and heats of vaporization, fusion and sublimation. Since the temperatures generally encountered in rockets and missiles fall in the range of 2000-5000°K the necessary thermodynamic properties for the exhaust products must be known in this temperature range.

The existence of thermodynamic data, whether theoretical or experimental, in the range of 20-600°K for a given compound is not sufficient to permit the accurate theoretical evaluation of a propellant system which, on combustion, might form this compound at temperatures of 3000°K. Extrapolation of thermodynamic data over these temperature spans, i.e., 600 to 3000°K, are usually inaccurate. Of even greater importance is the fact that a large number of species produced in the combustion of propellants do not even exist at lower temperatures and thus their properties can only be determined at the high temperatures where they exist. It is for these reasons that research programs have been undertaken to determine the physical and thermodynamic properties of those species expected to be formed by the combustion of propellants.

The current interest in the use of the light metals and their compounds (Li, Be, Mg, Al, B and their hydrides) as fuels or additives in solid or hybrid propellants, has prompted the inauguration of numerous research programs designed to determine the requisite thermodynamic and physical properties of compounds arising from interaction of the metals with the oxidizers employed (generally oxygen or fluorine compounds). Thus, species of prime interest are those arising from reaction of a metal ion with fluorine, oxygen, nitrogen or combinations of these atoms. The present investigation is concerned with the determination of some physical and thermodynamic properties of the compounds of Be with oxygen, fluorine and nitrogen.

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II. THERMODYNAMIC PROPERTIES OF $BeCl_2$

A. Background

The heat of formation of $BeCl_2(s)$ was first reported in 1921 by Mielenz and von Wartenberg.[1] The value of -122.6 ± 0.4 kcal/mole was obtained by the direct calorimetric determination of the heat of reaction of $Be(s)$ and $Cl_2(g)$. Siemonsen[2] reported a value of -109.2 ± 0.7 kcal/mole from bomb calorimetric measurements of the same reaction. More recently Johnson and Gilliland[3] at NBS obtained a calorimetric value of -118.03 ± 0.56 kcal/mole. This most recent calorimetric value has been substantiated by the work of Thompson, Sinke and Stull,[4] who obtained a value of $-117.56 \pm .50$ from the heat of solution of $Be(s)$ in HCl.

Inasmuch as the heat of formation $BeCl_2(g)$ has not been measured experimentally the value of -86.3 kcal/mole, currently used in the JANAF Tables, is based on calculations from the vapor pressure date of Rahlf and Fischer.[5] These vapor pressure data, which constitute the only data available, were obtained over the temperature range $340^{\circ} - 460^{\circ}C$ and pressures of $8 - 380$ mm, using manometric methods. The reliability of the data of Rahlf and Fischer is questionable since they indicated that a considerable reaction took place between their quartz reaction vessel and the $BeCl_2$.

However, Brewer[6] calculated the free energy of dimerization of $BeCl_2$ from the work of Rahlf and Fischer and has concluded that the dimer, Be_2Cl_4, is the important gaseous species from room temperature to the boiling point at 1 atm.

The present work has been undertaken to obtain definitive values for the heats of vaporization, sublimation and fusion of $BeCl_2$. The application of gravimetric and torsion effusion techniques and transpiration methods will facilitate the study of the vapor pressure at relatively low temperatures and will allow the calculation of the heat of dimerization.

B. Apparatus

1. Vacuum Systems

The determination of vapor pressures by either gravimetric or torsion effusion methods requires that the effusion cell be enclosed in a cavity in which the pressure is maintained at less than 10^{-2} times the vapor pressure to be measured. In order to achieve these low pressures a vacuum system shown in Fig. 4 has been constructed. This consists of two separate vacuum chambers, one capable of

achieving ultimate vacua of 10^{-6} mm Hg or lower and the other a bakable system capable of vacua of 10^{-9} mm Hg or lower.

2. Gravimetric Effusion Apparatus

The gravimetric effusion apparatus used in this work is similar in construction to that described earlier.[7] The effusion cell, machined from high density graphite, is attached to a calibrated quartz spring by a fine tungsten wire, 15" long. The spring is suspended from a fine tungsten wire attached to a magnetically operated winding drum located at the top of the vertical chamber. By manipulating the magnetic device the quartz spring and cell can be positioned vertically within the chamber.

The effusion cell and chamber are heated by means of a tape wrapped around the chamber. The temperature of the chamber is controlled by adjusting the power supplied to the heating tape through a variable auto transformer. The cell temperature is measured by a thermocouple imbedded in a graphite block placed in the chamber near the cell.

In order to prevent condensation of $BeCl_2$ on the quartz spring it has been found necessary to interpose several condensing rings between the cell and the quartz spring. The rings are supported at the flange where the cell chamber is attached to the vertical chamber. The fine wire attaching the cell to the spring passes through small holes in the center of the rings.

3. Torsion Effusion Apparatus

The apparatus used in this phase of the work is similar to that described earlier,[8] and consists of a fine torsion wire, to which the cell is attached, suspended from the top of the vertical chamber. The effusing gas imparts a torque to the cell and results in the rotational displacement of the cell about its axis. In order to measure the angle of displacement of the cell, a mirror is fixed to the cell holder; the change in the angles of incidence and reflection of the mirror is measured.

Temperature control and measurement are accomplished in the same manner as described above for the gravimetric effusion studies.

C. Experimental Procedure

1. General

The effusion cells used in this work are cleaned initially by washing with water and then are dried under vacuum. The cell is charged with $BeCl_2$ in a dry box and attached to the gravimetric spring or torsion wire. The system is then

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evacuated. The cell chamber is then heated to about 200°C for an hour to decompose any beryllium chloride-hydrate which may have formed by absorption of moisture.
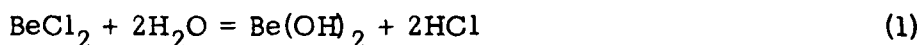
The cell chamber is then heated to the experimental temperature and the requisite measurements are made. In the gravimetric effusion experiments the rate of contraction of the calibrated quartz spring is measured using a Gaertner Cathetometer.

In the torsion effusion experiments, the angle through which the cell rotates is determined by measuring the angular displacement of the reflection of an object using a horizontal cathetometer.

The methods of calibrating the quartz springs and torsion wires have been discussed in earlier reports.[7,8]

2. Materials

Beryllium chloride (99.6%) was obtained from the Brush Beryllium Company as a fine crystalline product. This material is extremely hygroscopic and even very brief exposure to laboratory air results in the absorption of substantial amounts of moisture. Simple heating of the resulting "hydrated" material causes the elimination of HCl, by either reaction (1) or (2) below.

$$BeCl_2 + 2H_2O = Be(OH)_2 + 2HCl \tag{1}$$

$$BeCl_2 + H_2O = BeO + 2HCl \tag{2}$$

Efforts have been made to eliminate the difficulty introduced by the absorption of moisture. The material is handled only in a dry box; handling and exposure of the material even to the dry box atmosphere is minimized as much as possible.

Some evidence indicates that the material as obtained from the supplier has been exposed to moisture. Several samples of the material have been resublimed in this laboratory and experimental results using these samples appear to be more consistent than those using the material as supplied.

D. Preliminary Results

Extrapolation of the data of Rahlf and Fischer[5] from the experimental region of 340 - 460°C to lower temperatures indicated pressures of about 0.1 mm and 2 mm at 250 and 300°C respectively were to be expected. Preliminary data obtained

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in this laboratory (Table I), however, indicate pressures of about 0.01 mm and 0.2 mm at these same temperatures. The higher vapor pressures of Rahlf and Fischer[5] may be the results of their indicated reactions of $BeCl_2$ with quartz and the reactions (1) and (2) above.

On the basis of these preliminary experiments, an estimate of the heat of sublimation of $BeCl_2$ has been made. The second law heat of sublimation, obtained from the slope of a log P vs. 1/T plot, has a value of approximately 35 kcal/mole. A third law value of about 34 kcal/mole is obtained from the preliminary data. It should be noted that the value of the heat of sublimation reported here is only tentative and considerable uncertainty, approximately 5 kcal/mole, remains. These may be compared with the data of Rahlf and Fischer[5] which yield a second law value of 30 kcal/mole for the heat of sublimation of $BeCl_2(s)$ to monomeric $BeCl_2(g)$.

The possibility of reaction of $BeCl_2$ with the graphite has been considered. However, based on the preliminary work done to date, there has been no indication of reaction of these materials. More detailed studies of this reaction will be made before conclusion of the investigation.

The extremely hygroscopic nature of the fine crystalline $BeCl_2$ has been the source of considerable difficulty. Traces of moisture absorbed by the samples cause partial decomposition to the oxide (or hydroxide) when the sample is heated. As the effusion experiment proceeds and the $BeCl_2$ is lost from the mixture the concentration of impurity increases and interferes with the establishment of the equilibrium between solid and vapor in the cell. In other words, as the concentration of the impurity in the mixture increases the accommodation coefficient decreases.

Inspection of equation (3) below, which relates the equilibrium pressure P_{eq} to the experimentally determined pressure P, demonstrates that as the accommodation coefficient, $\propto$, decreases the experimental pressure also decreases.

$$ P = \frac{P_{eq}}{1 + \frac{a}{\propto A}} \tag{3} $$

where a = total orifice area and
A = surface area of material.

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In the course of this study it has been noted that the experimental pressures are markedly dependent on both the temperature and the duration of the heating time. For example, at high temperatures, where the $BeCl_2$ effuses at a rapid rate, a rapid decrease in the rate of weight loss is noted. On the other hand, at low temperatures, where $BeCl_2$ effuses slowly, the rate of weight loss remains relatively constant or decreases very slowly.

The interference of the impurity in the $BeCl_2$ has been confirmed in several recent experiments in which resublimed $BeCl_2$ was used. In these cases the experimentally determined pressures were substantially higher than those obtained earlier using $BeCl_2$ as supplied. Further experiments are in progress with this high purity material. Experiments varying the orifice size for determination of the accommodation coefficient and torsion measurements to determine the molecular weight (whether $BeCl_2(g)$ exists in monomeric or dimeric form) of effusing gas are also contempleted.

III. THERMODYNAMIC PROPERTIES OF BeCl(g).

A. Background

The first spectroscopically determined dissociation energy (D_o^o) value for the BeCl species was accomplished by Fredrickson and Hogan[9] in 1934. By using new physical constants and conversion factors Herzberg[10] in 1950 recalculated from the original data a new D_o^o value of 4.2 electron volts (ev.). To this value Gaydon applied corrections dependent on the ionic character of BeCl and obtained a value of 3.0 ev. In 1960, Novikov and Tunitskii[11] determined a new value of 5.9 ± 0.5 ev. for the dissociation energy of BeCl. Adjusting the dissociation energy values of BeCl to standard conditions, one calculates the values for the heat of formation $(\Delta H_f^{298^o K})$ of BeCl as shown in Table I.

In a previous investigation[12] a thermochemical determination yielded definitive values for ΔH_f and S of BeF (g). A similar equilibrium study of the heat of reaction of beryllium metal with gaseous beryllium chloride has been undertaken for the chloride as shown by the reaction.

$$BeCl_{2(g)} + Be_{(s)} \longrightarrow 2 BeCl_{(g)} \qquad (4)$$

B. Apparatus and Procedure

To study the equilibrium of gaseous $BeCl_2$ with solid and liquid Be, the effusion apparatus (Fig. 1) and the vacuum-resistance furnace (Fig. 2) were constructed. The effusion cell, containing the high purity beryllium metal, was constructed from a tube of beryllium oxide obtained from the Brush Beryllium Company. An effusion hole of 0.7 mm diameter was drilled through the side of the tube approximately one half centimeter from the closed end. A graphite adapter with a 2 mm hole connected the effusion cell to the delivery tube in order to permit gaseous $BeCl_2$ 'o enter the effusion cell. The delivery tube was constructed of beryllium oxide. A nickel boat containing high purity $BeCl_2$ (described previously) was placed in the delivery tube at the point most distant from the furnace. The delivery tube was closed off with a graphite plug. The vacuum-resistance furnace has been described previously.[12]

Due to the hygroscopic nature of $BeCl_2$ as explained in Section II experimental procedures were designed to minimize the contact of $BeCl_2$ with moisture. The reaction materials, beryllium and beryllium chloride, were weighed

and placed into the effusion apparatus in a dry box. The effusion apparatus was then quickly placed in the resistance furnace and evacuated. During this procedure the effusion apparatus came in contact with moisture in the air. Since the only entrance to the effusion apparatus was the effusion hole, the diffusion of water vapor into the apparatus was considered unlikely. After evacuating the system to less than a micron, the furnace was turned on and slowly brought up to the desired temperature. The $BeCl_2$ boat was heated by conduction down the delivery tube from the hot zone of the resistance furnace. In future experiments heat conduction will be controlled by a cooling coil. After a selected period of time the furnace was cooled and the container weighed.

C. Preliminary Results

Four determinations of reaction (4) have been carried out in a temperature range of 1175 to 1450°C. These data are presented in Table 3. Based on these data a tentative value for the heat of reaction of 67 ± 5 kcal/mole is obtained based on the method of calculation described in detail in the 4th Quarterly Report.[12] Employing the data in the JANAF Tables for the species involved in reaction (4) a preliminary value of -10 ± 5 kcal/mole is obtained for ΔH_{f298} of $BeCl(g)$. This value may be more positive by 2 to 3 kcal since the ΔH_f of $BeCl_2(g)$ reported in the JANAF Tables is based on the sublimation value of Rahlf and Fischer, which appears to be in considerable error.

IV. THERMODYNAMIC PROPERTIES OF BeO(s)

A. Background

Reliable data on the heat capacity of BeO through its crystalline and into its liquid range is currently not available. Since BeO melts in the neighborhood of $2800°K \pm 50°K$,[13,14] a furnace and calorimeter combination which can produce and withstand temperatures to at least $3000°K$ is necessary.

A considerable amount of work has been performed on the physical and thermodynamic properties of BeO.[15,16] The heat of formation has been calculated from measured heat of combustion.[17,18] Vapor pressures were determined at temperatures up to $2150°C$.[19] However all available specific heat data has been determined at temperatures below $2200°K$.[20,21] No direct measurements of the heat of fusion of BeO have been reported in the literature to date.

B. Apparatus

In order to determine the heat of fusion and the high temperature heat capacities of BeO, an electron bombardment furnace-calorimeter combination has been designed and constructed. The calorimeter is patterned after the Southard type designed and constructed by the National Bureau of Standards,[22,23] and has been successfully employed by Hoch and Johnston.[24,25]

The furnace-drop-calorimeter combination is essentially an evacuated isothermal calorimeter system surmounted by a furnace where the substance is heated to the desired temperature under vacuum. (Figs. 3,5) The furnace and calorimeter are connected by a single tube through which the sample "drops" to the calorimeter well after heating. Within the tube is a pair of "heat locks" which are opened long enough to permit passage of the sample then closed quickly to prevent heat leak from the furnace. Dropping to the bottom of the well, the sample releases heat which melts a portion of a pre-formed mantle of ice surrounding the tube. The change in the volume of water is measured externally by a calibrated mercury column which is sensitive to the water-ice equilibrium by direct contact. It should be noted that the basic isothermal ice calorimeter was first developed over half a century ago and, except for improvements due to the better materials available for construction, has been used over the years with only slight changes to suit the experimenter's needs.[26,29]

Major changes in the furnace-calorimeter system of NBS consist in an electron bombardment furnace which can produce higher temperatures over a small area with considerably greater facility than was possible in the past with more conventional heating equipment. The performance of the electron bombardment furnace has been improved over our earlier models by more complete shielding around the heating coil and sample. There are now four cylindrical molybdenum shields and two funnel-shaped tantalum shields in use. Increased shielding provided higher temperatures with low current and voltage. The sample dropping technique was developed to provide greater accuracy. A guide tube was installed to prevent the sample from swinging in a large arc while heating. When released, the sample will not fall out of range of the drop tube. A photograph of the entire assembly is shown in Fig. 5.

A cell to hold the BeO for heat of fusion measurements was made. In choosing materials for construction of the sample cell, it was necessary to consider temperature requirements and possible reaction of the compound with the material used. The possible materials with melting points above that of BeO are molybdenum, tantalum, rhenium, carbon and tungsten. Of these, reactions occur with tantalum,[30] carbon and tungsten.[31] Molybdenum melts below 2900°K which makes it unsuitable for use in liquid BeO measurements. Experiments to determine whether rhenium reduces BeO at high temperatures resulted in no noticeable reaction. Based on these results, a rhenium-lined tantalum cell will be employed for the measurements of the heat of fusion of BeO.

V. FUTURE WORK

During the next report period the measurements necessary to determine the heat of formation and entropy of $BeCl(g)$ and the heat of sublimation of $BeCl_2$ will be completed. The molecular weight of the vapor effusing from the cell in which $BeCl_2$ measurements are being made will be established by means of the torsion effusion procedure. The heat of fusion of BeO will be determined and measurements of the heat capacity of BeO(s) between 1800°C and the melting point will be commenced.

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TABLE I

PRELIMINARY DATA ON THE VAPOR PRESSURE OF $BeCl_2$

$T^{O}K$	$P_{mm} \times 10^3$
499	1.64
510	2.61
522	4.25
537	6.98
524	3.57
512	1.62
519	7.5
531	11.3
535	10.3
554	14.7
487	1.2
545	12.9
573	179.0
562	39.2
562	38.3
535	8.0
543	36.6
552	43.9
574	56.2
542	30.4
554	42.5
568	52.7
575	75.8

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TABLE II

HEATS OF FORMATION OF BeCl(g)
DERIVED FROM SPECTROSCOPIC DATA

AUTHOR	D_o^o (ev)	ΔH_f^{298} kcal/mole
Fredrickson (Herzberg Correction)	4.2	+ 9.46
Fredrickson (Gaydon Correction)	3.0	+37.14
Novikov and Tunitskii	5.9 $\pm$ 0.5	-29.72

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TABLE III

PRELIMINARY DATA ON THE REACTION OF
$BeCl_2(g)$ WITH $Be(s,l)$ TO YIELD $BeCl(g)$

$T^{\circ}K$	Wt. $BeCl_2$ Lost, mg	Wt. Be Lost, mg*
1450	658.0	3.0
1500	678.2	7.0
1560	743.0	9.2
1675	302.1	16.0

* Corrected for weight lost due to vaporization of Be.

(A) Graphite plug
(B) Nickel boat containing BeCl$_2$
(C) Beryllium oxide delivery tube
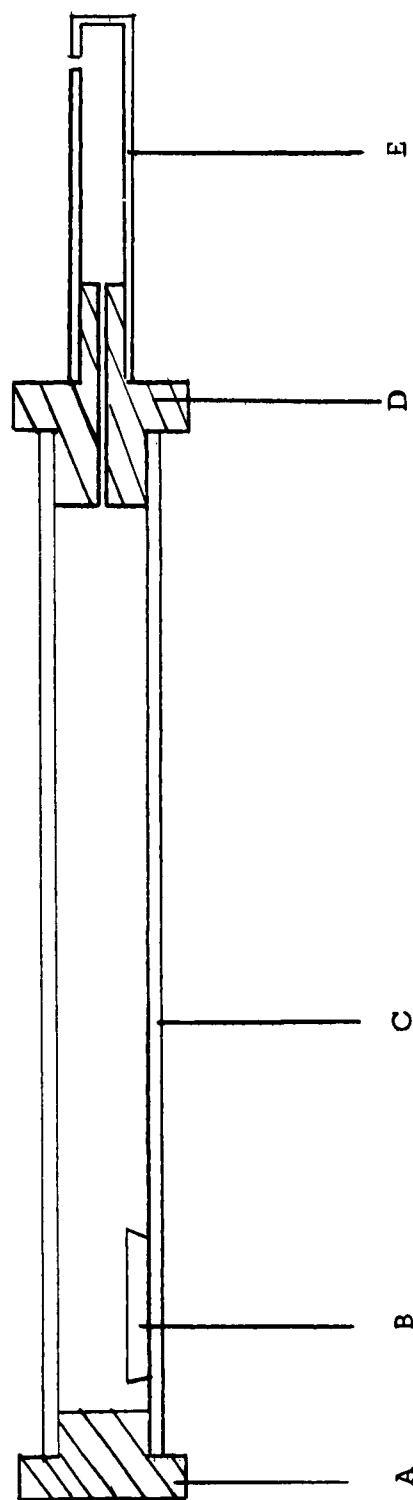(D) Graphite adapter with 2 mm hole
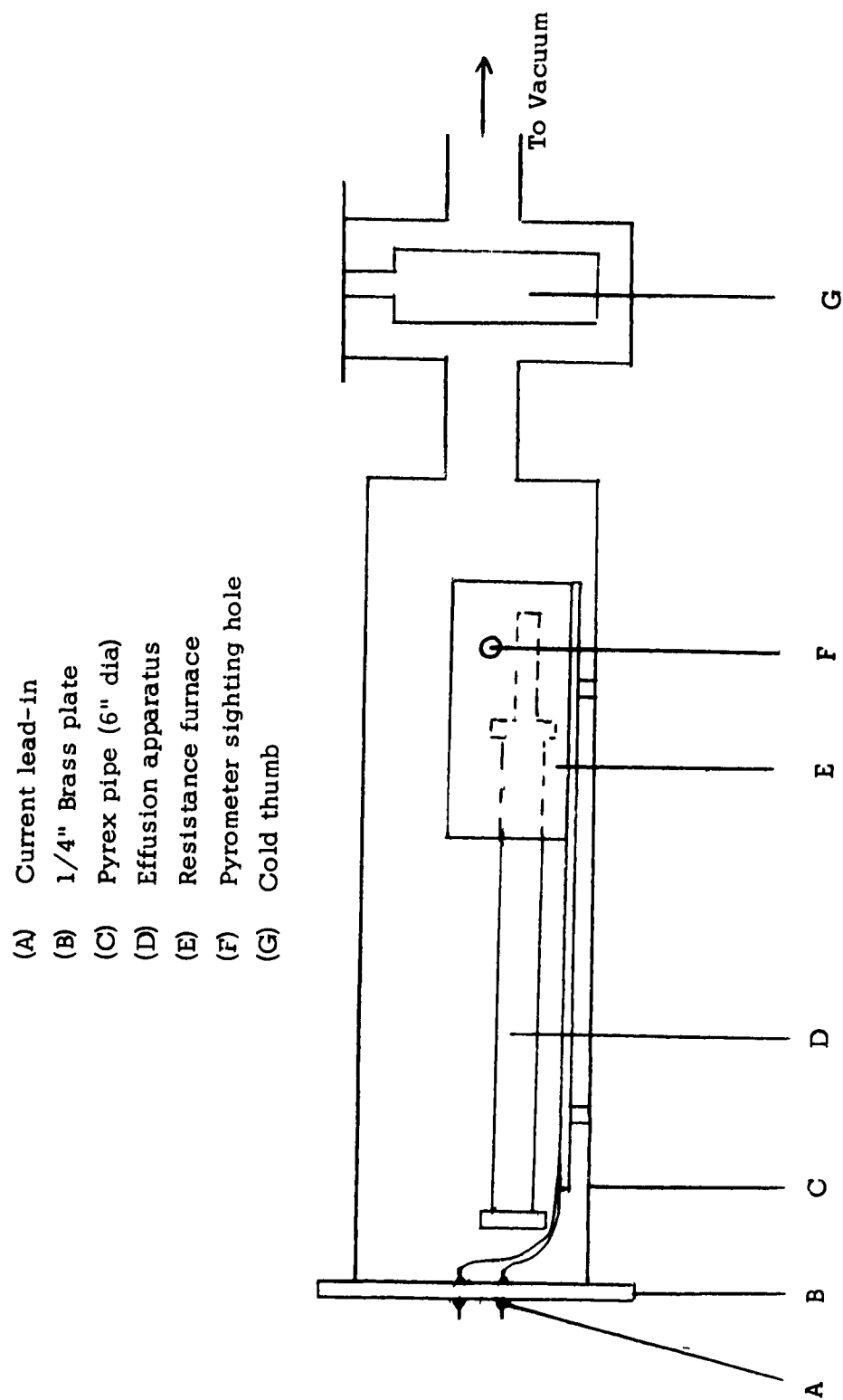(E) Beryllium oxide effusion tube

Fig. 1. Effusion Apparatus

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(A) Current lead-in
(B) 1/4" Brass plate
(C) Pyrex pipe (6" dia)
(D) Effusion apparatus
(E) Resistance furnace
(F) Pyrometer sighting hole
(G) Cold thumb

To Vacuum

A B C D E F G

Fig. 2. Vacuum Resistance Furnace and Effusion Apparatus

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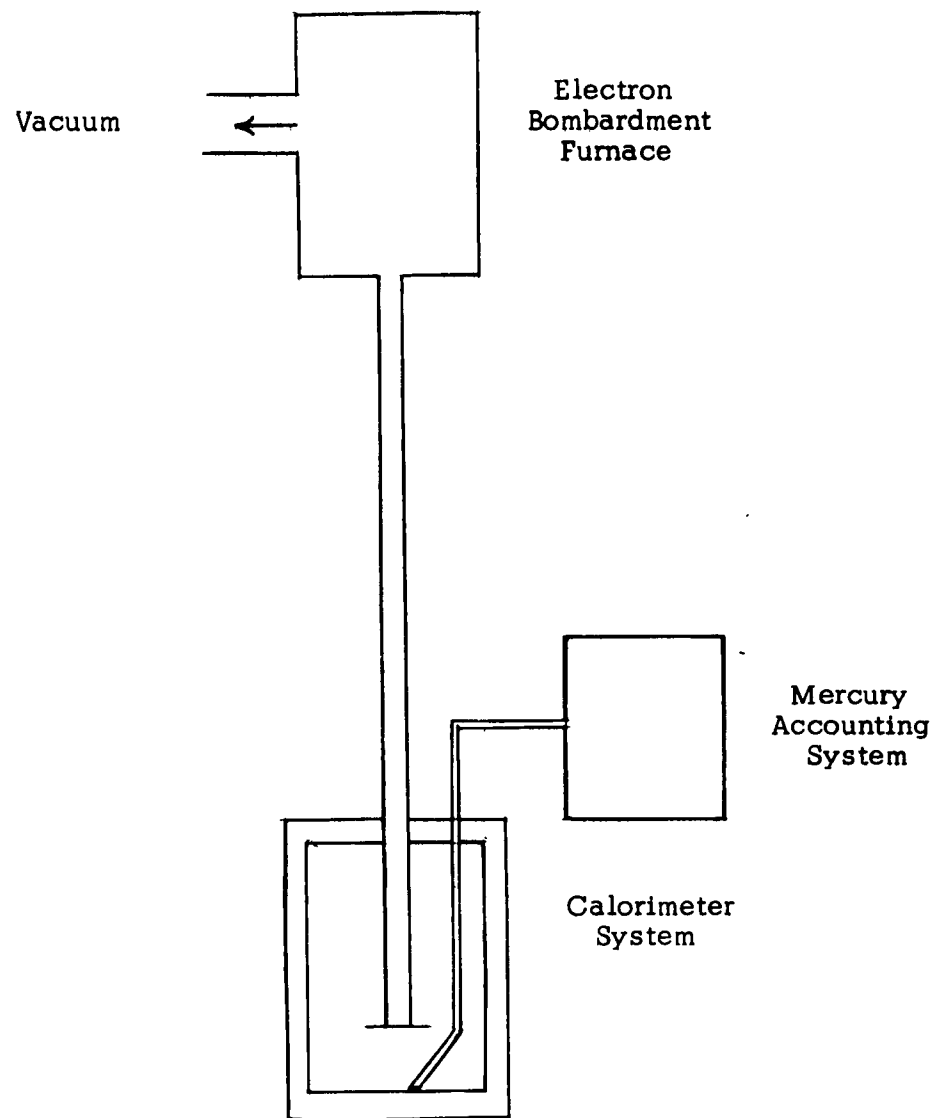Fig. 3. Furnace--Drop Calorimeter System
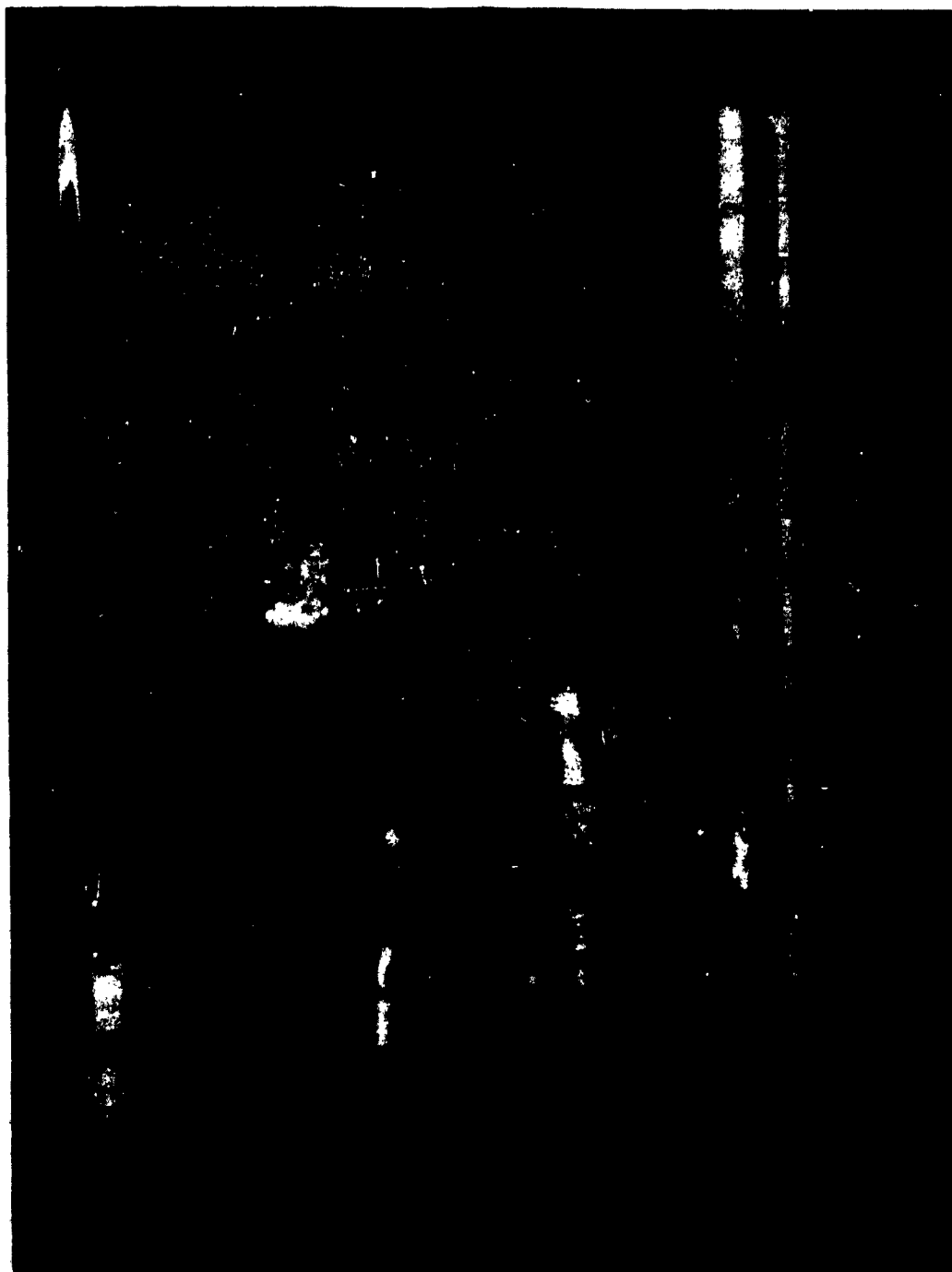
Fig . 4 . Ultra High Vacuum Torsion and Gravimetric Apparatus

Fig. 5. Electron Bombardment
Calorimeter Apparatus

Fig. 6. High Temperature Molecular
Flow Effusion Apparatus